Equation Forms in Process Modelling Continued

Ordinary Differential Equations - Initial Value Problem (ODE-IVP)

For most of the processing systems of interest to the chemical engineer, there are three fundamental quantities :mass, energy and momentum. These quantities can be characterized by variables such as density, concentration, temperature, pressure and flow rate. These characterizing variables are called as state of the processing system. The equations that relate the state variables (dependent variables) to the independent variables are derived from application of conservation principle on the fundamental quantities and are called the state equations.

Let quantity S denote any one of the fundamental quantities

- Total mass
- Mass of the individual components
- Total energy.
- Momentum

Then, the principles of the conservation of the quantity S states that:

$$\frac{\text{Accumulation of S within a system}}{\text{Time Period}} = \frac{\text{Flow of S in the system}}{\text{Time Period}} - \frac{\text{Flow of S out of the system}}{\text{Time Period}} + \frac{\text{Amount of S generated within the system}}{\text{Time Period}} - \frac{\text{Amount of S consumed within the system}}{\text{Time Period}}$$

Figure 6 shows schematic diagram of a general system and its interaction with external world. Typical dynamic model equations are as follows:

Total Mass Balance

$$d(\rho V) = \sum_{i:inlet} \rho_i F_i - \sum_{j:outlet} \rho_j F_j$$

Mass Balance of the component A

$$\frac{dn_a}{dt} = \frac{d(C_a V)}{dt} = \sum C_{ai} F_i - \sum C_{aj} F_i \ - rV \qquad \text{----(30)}$$

Total energy Balance

$$\frac{dE}{dt} = \frac{d(U+K+P)}{dt} = \sum \rho_i F_i h_i - \sum \rho_j F_j h_j \pm Q \pm W_S \simeq \frac{dH}{dt}$$

Variables and parameters appearing in these equations are are described in Table Table 3.

By convention, a quantity is considered positive if it flows in and negative if it flows out. The state equations with the associated variables constitute a 'lumped parameter mathematical model' of a process, which yields the dynamic or static behavior of the process. The application of the conservation principle stated above will yield a set of differential equations with the fundamental quantities as the dependent variables and time as independent variable. The solution of the differential equations will determine how the state variables change with time i.e., it will determine the dynamic behavior of the process. The process is said to be at the steady state if the state variables do not change with time. In this case, the rate of accumulation of the fundamental quantity S is zero and the resulting balance yields a set of algebraic equations

Table 3: Description of Variables and Parameters

i	inlet
j	outlet
ρ	Density of the material in the system

ρ_i	Density of the material in the i'th inlet stream
ρ_j	Density of the material in the j'th outlet stream
V	Total volume of the system
F_i:	Volumetric flow rate of the i'th inlet stream
F_j:	Volumetric flow rate of the j'th outlet stream
n_a	Number of moles of the component A in the system
C_A	Molal concentration (moles /volume)of A in the system
C_{Ai}	Molal concentration (moles /volume)of A in the i'th inlet stream
C_{Aj}	Molal concentration (moles /volume)of A in the j'th outlet stream
r	Reaction rate per unit volume of the component A in the system.
h_i	Specific enthalpy of the material in the i'th inlet stream
h_i	Specific enthalpy of the material in the j'th outlet stream
U, K, P	Internal, kinetic and potential energies of the system, respectively.
Q	Amount of the heat exchanged between the system and the surroundings per unit time
W_S	Shaft work exchanged between the system and its surroundings.

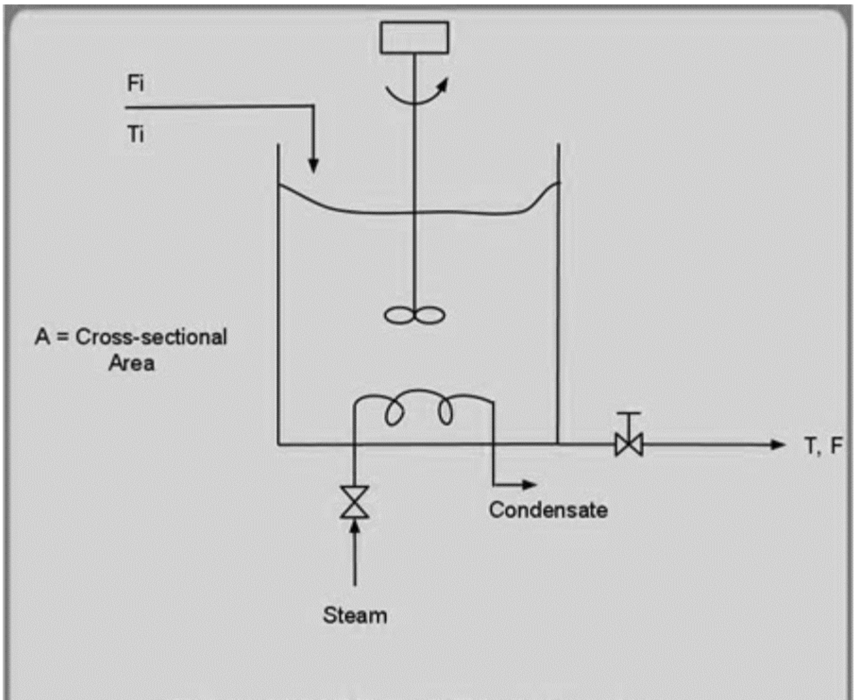

Figure 7: Stirred Tank Heater

Example 5

Stirred Tank Heater System (Figure 7): Total momentum of the system remains constant and will not be considered. Total mass balance: Total mass in the tank at any time t $= \rho V = \rho A h$ where A represents cross sectional area.

----(31)

$$\frac{d(\rho Ah)}{dt} = \rho F_i - \rho F$$

Assuming that the density is independent of the temperature,

$$A\frac{dh}{dt} = F_i - F \qquad \text{----(32)}$$

Now, flow out due to the gravity is also a function of height

$$F = k\sqrt{h} \qquad \text{-}$$

Thus,

$$A\frac{dh}{dt} + k\sqrt{h} = F_i \qquad \text{---(33)}$$

Total energy of liquid in the tank is given by

$$E = U + k + P$$

However, since tank does not move

$$\frac{dk}{dt} = \frac{dP}{dt} = 0\ ;\quad \frac{dE}{dt} = \frac{dU}{dt}$$

For liquid systems

$$\frac{dU}{dt} \approx \frac{dH}{dt} \qquad \text{----(34)}$$

where H is total enthalpy of the liquid in the tank.

$$H = \rho VC_p(T - T_{ref}) = \rho AhC_p(T - T_{ref}) \qquad \text{----(35)}$$

T_{ref} represents reference temperature where the specific enthalpy of the liquid is assumed to be zero. Now, using the energy conservation principle

$$\frac{d(\rho AhC_p(T - T_{ref}))}{dt} = \rho F_iC_p(T_i - T_{ref}) - \rho FC_p(T - T_{ref}) + Q \qquad \text{----(36)}$$

where Q is the amount of heat supplied by the steam per unit time. Assuming $T_{ref} = 0$, we have

$$A\frac{d(hT)}{dt} = F_iT_i - FT + \frac{Q}{\rho C_p} \qquad \text{----(37)}$$

$$\begin{aligned} A\frac{d(hT)}{dt} &= Ah\frac{dT}{dt} + AT\frac{dh}{dt} \\ &= Ah\frac{dT}{dt} + T(F_i - F) \\ &= F_iT_i - FT + \frac{Q}{\rho C_p} \end{aligned}$$

Or

$$Ah\frac{dT}{dt} = F_i(T_i - T) + \frac{Q}{\rho C_p}$$

Summarizing modelling steps

$$\frac{dh}{dt} = \frac{1}{A}(F_i - F) = \frac{1}{A}(F_i - k\sqrt{h}) \qquad \text{----(38)}$$

$$\frac{dT}{dt} = \frac{F_i}{Ah}(T_i - T) + \frac{Q}{Ah\rho C_p} \qquad \text{---(39)}$$

The associated variables can be classified as

- **state(**ordependent) variables : h, T
- **Input (**orindependent) variables : T_i, F_i, Q
- **Parameters**: A, ρ, C_p

Steady state behavior can be computed by solving following two equations

$$\frac{dh}{dt} = F_i - k\sqrt{h} = 0 \qquad \text{----(40)}$$

$$\frac{dT}{dt} = \frac{F_i}{Ah}(T_i - T) + \frac{Q}{\rho C_p} = 0 \qquad \text{----(41)}$$

Once we choose independent variables $F_i = \overline{F}_i, T_i = \overline{T}_i$ and $Q = \overline{Q}$, the steady state $h = \overline{h}$ and $T = \overline{T}$ can be computed by simultaneously solving nonlinear algebraic equations (41-42).

The system will be disturbed from the steady state if the input variables suddenly change value at $t = 0$. Consider following two situations in which we need to investigate transient behavior of the above process

- T_i decreases by 10% from its steady state value $\overline{T}_i$ at $t = 0$. Liquid level remains at the same steady state value as T_i does not influence the total mass in tank. The temperature T in the tank will start decreasing with time (see Figure 8). How $T(t)$ changes with time is determined by the solution of the equation (38) using the initial as condition $T(0) = \overline{T}$, the steady state value of T.
- F_i is decreased by 10% from its steady state value $\overline{F}_i$: Since F_i appears in both the dynamic equations, the temperature and the liquid level will start changing simultaneously and the dynamics will be governed by simultaneous solution of coupled nonlinear differential equations (38-39) starting with initial conditions $T(0) = \overline{T}, h(0) = \overline{h}$. Figure 9 show schematic diagrams of the process responses for step change in F_i.

  It is also possible to investigate response of the system for more complex inputs, such as

$$T_i(t) = \overline{T}_i + \Delta T_i \sin(\omega t)$$

where above function captures daily variation of cooling water inlet temperature. In each case, the transient behavior $T(t)$ and $h(t)$ is computed by solving the system of ODEs subject to given initial conditions and time variation of independent inputs (i.e. forcing functions).

Example 6

Three isothermal CSTRs in series: Consider three isothermal CSTRs in series in which

a first order liquid phase reaction of the form $A \rightarrow B$ is carried out. It is assumed that volume and liquid density remains constant in each tank and

$$V_1 \frac{dC_{A1}}{dt} = F(C_{A0} - C_{A1}) - kV_1 C_{A1} \quad \text{----(42)}$$

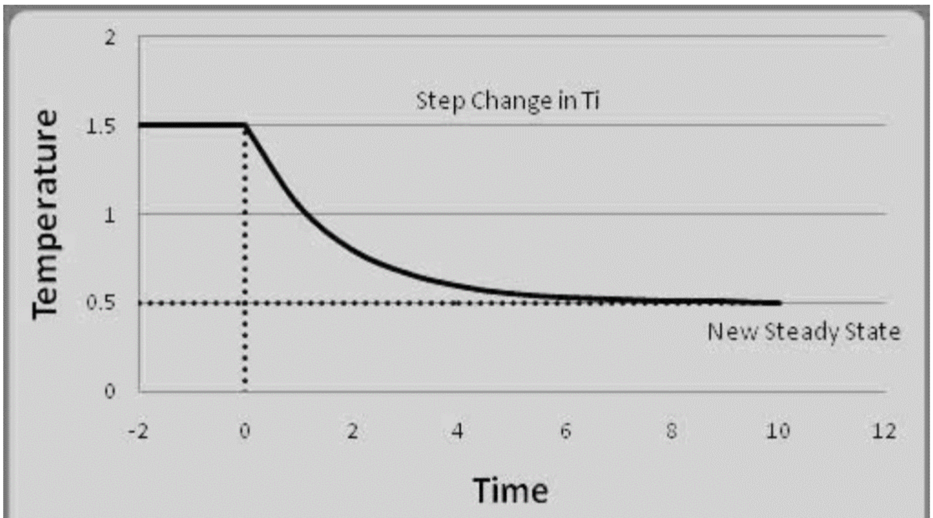

Figure 8: Temperature Response

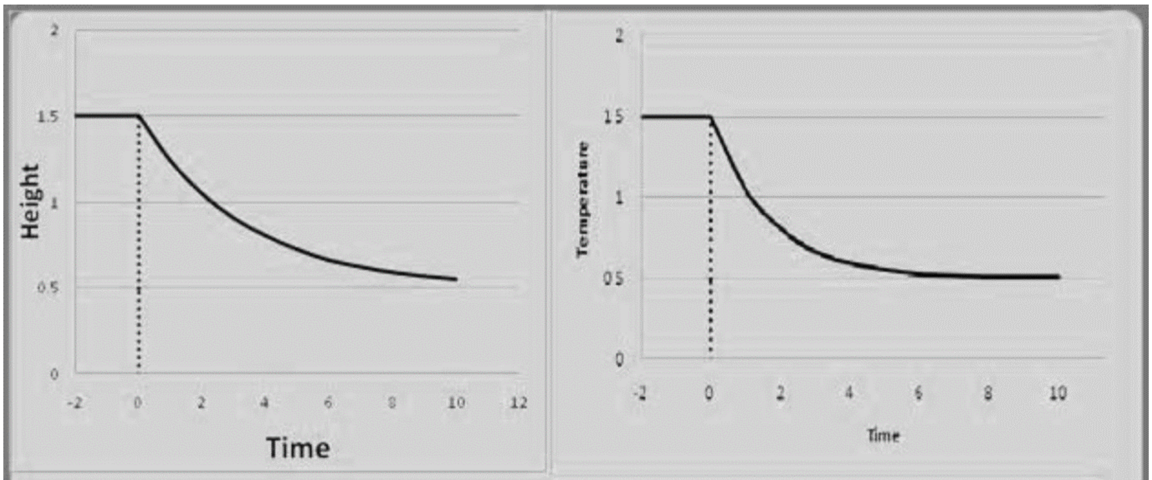

Figure 9: Dynamic Response to Step Change in Fi

$$V_2 \frac{dC_{A2}}{dt} = F(C_{A1} - C_{A2}) - kV_2 C_{A2} \quad \text{----(43)}$$

$$V_3\frac{dC_{A3}}{dt} = F(C_{A2} - C_{A3}) - kV_3C_{A3} \quad ----(44)$$

Defining $\tau = F/V,$ we can re arrange the above set of equations as

$$\frac{d}{dt}\begin{bmatrix} C_{A1} \\ C_{A2} \\ C_{A3} \end{bmatrix} = \begin{bmatrix} -(k+1/\tau_1) & 0 & 0 \\ 1/\tau & -(k+1/\tau_2) & 0 \\ 0 & 1/\tau & -(k+1/\tau_3) \end{bmatrix}\begin{bmatrix} C_{A1} \\ C_{A2} \\ C_{A3} \end{bmatrix} + \begin{bmatrix} 1/\tau_1 \\ 0 \\ 0 \end{bmatrix}C_{A0} \quad ----(45)$$

$$\mathbf{x} = [C_{A1}, C_{A2}, C_{A3}]^T$$
$$\frac{d\mathbf{x}}{dt} = A\mathbf{x} + BC_{A0} \quad ----(46)$$

where matrices A and B are defined in the above equation. Now, suppose initially $C_{A0} = \bar{C}_{A0},$ till $t = 0$, and, for $t \geq 0$, C_{A0} was changed to $C_{A0} = 0$. Then we are required to solve

$$\frac{d\mathbf{x}}{dt} = A\mathbf{x}; \qquad \mathbf{x} = \mathbf{x}(0) \quad at \quad t = 0 \quad ----(47)$$

and generate trajectories $\mathbf{x}(t)$ (i.e. $C_{A1}(t), C_{A2}(t)$ and $C_{A3}(t)$) over interval $[0, t_f]$. This is a typical problem of dynamic simulation of lumped parameter system.

Example 7

Continuous Fermenter: Consider a continuously operated fermenter described by the following set of ODEs

$$\frac{dX}{dt} = F_1(X, S, P, D, S_f) = -DX + \mu X \quad ----(48)$$

$$\frac{dS}{dt} = F_2(X, S, P, D, S_f) = D(S_f - S) - \frac{1}{Y_{X/S}}\mu X \quad ----(49)$$

$$\frac{dP}{dt} = F_3(X, S, P, D, S_f) = -DP + (\alpha\mu + \beta)X \quad ----(50)$$

where X represents effluent cell-mass or biomass concentration, S represents substrate concentration and P denotes product concentration. It is assumed that product concentration (S) and the cell-mass concentration (X) are measured process outputs while dilution rate (D) and the feed substrate concentration (S_f) are process inputs which can be manipulated. Model parameter μ represents the specific growth rate, $Y_{X/S}$ represents the cell-mass yield, α and β are the yield parameters for the product. The specific growth rate model is allowed to exhibit both substrate and product inhibition:

$$\mu = \frac{\mu_m(1 - \frac{P}{P_m})S}{K_m + S + \frac{S^2}{K_i}} \quad ----(51)$$

where μ_m represents maximum specific growth rate, P_m represents product saturation constant, K_m

substrate saturation constant and the K_i represents substrate inhibition constant. Defining state and input vectors as

$$\mathbf{x} = \begin{bmatrix} X & S & P \end{bmatrix}^T \; ; \; \mathbf{u} = \begin{bmatrix} D & S_f \end{bmatrix}^T \qquad \text{----(52)}$$

the above equation can be represented as

$$\frac{d\mathbf{x}}{dt} = F(\mathbf{x}, \mathbf{u}) \qquad \text{----(53)}$$

A typical problem dynamic simulation problem is to find trajectories of product, biomass and substrate concentrations over an interval $[0, t_f]$, given their initial values and dilution rate $D(t)$ and feed substrate concentration S_f as a function of time over $[0, t_f]$.

In abstract terms, the dynamic simulation problem can be states as follows. Given time trajectories of independent variables $\{\mathbf{u}(t) : 0 \leq t \leq t_f\}$, and initial state, $\mathbf{x}(0)$), of the system, obtain state trajectories $\{\mathbf{x}(t) : 0 \leq t \leq t_f\}$ by integrating

$$\frac{d\mathbf{x}}{dt} = F[\mathbf{x}(t), \mathbf{u}(t)] \; ; \; \mathbf{x} = \mathbf{x}(0) \text{ at } t = 0 \qquad \text{----(54)}$$

where $\mathbf{x} \in R^n$ represents dependent or state variables and $\mathbf{u} \in R^m$ denote independent inputs. As the independent variable trajectories are known *a-priori* while solving ODE-IVP, the problem can be looked at as n-ODE's in n variables with variable coefficients. Thus, the above problem can be re-stated as

$$\frac{d\mathbf{x}}{dt} = F_u(\mathbf{x}, t) \; ; \qquad \mathbf{x}(0) = \mathbf{x}_0 \qquad \text{----(55)}$$

In other words, a forced dynamic systems can be looked upon as unforced systems with variable parameters.

The model we considered above did not contain variation of the variables with respect to space. Such models are called as 'Lumped parameter models' and are described by ordinary differential equations of the form

$$\frac{dx_1}{dt} = f_1(x_1(t), x_2(t), \ldots, x_n(t), u_1(t), u_2(t), \ldots, u_m(t)) \qquad \text{----(56)}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\frac{dx_n}{dt} = f_n(x_1(t), x_2(t), \ldots, x_n(t), u_1(t), u_2(t), \ldots, u_m(t)) \qquad \text{----(57)}$$

$$x_1(0) = \overline{x}_1, \ldots, x_n(0) = \overline{x}_n \quad \text{(Initial conditions)}$$

where $x_1, \ldots, x_n$ denote the state (or dependent) variables and $u_1(t), \ldots, u_n(t)$ are denote independent inputs (or forcing functions) specified for $t >= 0$. Using vector notation, we can write the above set of ODEs in more compact form

$$\frac{d\mathbf{x}}{dt} = F(\mathbf{x}, \mathbf{u}) \qquad \text{----(58)}$$

$$\mathbf{x}(0) = \mathbf{x}_0 \qquad \text{----(59)}$$

where

----(60)

$$\mathbf{x}(t) = [x_1(t) \ldots x_n(t)]^T \in R^n$$

$$\mathbf{u}(t) = [u_1(t).....u_n(t)]^T \in R^m \qquad \text{----(61)}$$

$$F(\mathbf{x},\mathbf{u}) = [f_1(\mathbf{x},\mathbf{u})........f_n(\mathbf{x},\mathbf{u})]^T \in R^n \qquad \text{----(62)}$$

and $\mathbf{u}(t)$ is a forcing function vector defined over $t \geq= 0.$

- *Steady State Simulation Problem:* If we fix independent inputs to some constant value, say $\mathbf{u}(t) = \overline{\mathbf{u}}$ for $t \geq 0$, then we can find a steady state solution $\mathbf{x} = \overline{\mathbf{x}}$ corresponding to these constant inputs by simultaneously solving n nonlinear algebraic equations

$$F(\mathbf{x},\overline{\mathbf{u}}) = \overline{0} \qquad \text{----(63)}$$

obtained by setting $d\mathbf{x}/dt = \overline{0}$ where $\overline{0}$ represents $n \times 1$ zero vector.

- *Dynamic Simulation Problem:* Given input trajectories

$$\mathbf{u}(t) = [u_1(t) \quad u_2(t)..........u_m(t)]^T \qquad \text{----(64)}$$

as a function of time for $t \geq 0$ and with the initial state $\mathbf{x}(0)$, integrate

$$\frac{d\mathbf{x}}{dt} = F(\mathbf{x},\mathbf{u}(t)) \qquad \text{----(65)}$$

over interval $0 \leq t \leq t_f$ to determine state trajectories

$$\mathbf{x}(t) = [x_1(t) \quad x_2(t)..........x_n(t)]^T \qquad \text{----(66)}$$

Since $\mathbf{u}(t)$ is a known function of time, we re-state the above problem as

$$\frac{d\mathbf{x}}{dt} = F_{\mathbf{u}}(\mathbf{x},t) \ ; \ \mathbf{x}(0) = \mathbf{x}_0 \qquad \text{----(67)}$$

$F_{\mathbf{u}}(\mathbf{x},t)(= F(\mathbf{x},\mathbf{u}(t)))$ denotes $F()$ with the given $\mathbf{u}(t).$

2.5 Differential Algebraic Equations

Another important class of problems that arise in process engineering is a set of coupled differential algebraic equations. In this section, we discuss two examples belonging to this class.

Example 8

The process is a continuously stirred tank reactor, where a feed with unknown pH is flowing into the reactor. We add a basic solution, with known molarity, to the reactor to maintain the pH at a desired level. The flow-rate of the basic solution is the manipulated variable. The process is modelled using the following set of DAEs:

$$\frac{VdN^+}{dt} = m \times Cr - (F+m)N^+ \qquad \text{----(68)}$$

$$[H^+]^3 + (Ka + N^+)[H^+]^2 +$$
$$(N^+Ka - Kw - KaU)H^+ - KaKw = 0 \qquad \text{----(69)}$$

where N^+ is the concentration of the cation of the base in the CSTR and is the differential state, while hydrogen ion concentration, (H^+), is the algebraic state.

Table 4 : pH Balance Problem : Parameters and Initial Conditions

Parameter	Value
Equilibrium constant for water Kw	10^{-14}
Relative strength of acid mixture in the CSTR Ka	0.001
Feed rate to the tank F	13 L/min
Flow rate of the base m	15 L/min
Concentration of the base solution Cr	1 equiv/L
Concentration of the acid and its salts U	0.13 mol/L
Volume of tank V	90 L
Variable	**Initial Value**
N^+	0.005
H^+	0.086
N^+	0.01
H^+	0.0068

Example 9

The system presented here models the galvanostatic charge process of a thin film nickel hydroxide electrode. The rate of change of the mole fraction of nickel hydroxide is (y_1) given by

$$\frac{\rho V}{W}\frac{dy_1}{dt} = \frac{j_1}{F} \qquad \text{----(70)}$$

$$j_1 + j_2 - i_{app} = 0 \qquad \text{----(71)}$$

where

$$j_1 = i_{o1}[2(1-y_1)\exp(\frac{0.5F}{RT}(y_2 - \Phi_{eq,1})) - 2y_1 \times \exp(\frac{-0.5F}{RT}(y_2 - \Phi_{eq,1}))] \qquad \text{----(72)}$$

$$j_2 = i_{o2}[\exp(\frac{F}{RT}(y_2 - \Phi_{eq,2})) - \exp(\frac{-F}{RT}(y_2 - \Phi_{eq,2}))] \qquad \text{----(73)}$$

where y_2 is the potential difference at the solid liquid interface. (species) is the species balance while (charge) denotes the charge balance. j_1 and j_2 are derived from Butler-Volmer kinetics. The parameters and initial conditions are summarized in Table 5.

Table 5 : Ni-H electrode problem : Parameters and Initial Conditions

Parameter	Value
Faraday's Constant F	96487 C/mol
Ideal Gas Constant R	8.314 J/molK
Temperature T	298.15K
Equilibrium potential for nickel reaction $\varphi_{eq,1}$	0.420V
Equilibrium potential for nickel reaction $\varphi_{eq,2}$	0.303V
Density of Nickel ρ	$3.4 g/cm^3$
Molecular weight W	92.7 g/mol
Effective length V	1×10^{-5}cm

Applied Current Density on Nickel electrode i_{app}	1×10^{-5} A/cm^2
Exchange Current Density of Nickel Reaction i_{o1}	1×10^{-4} A/cm^2
Exchange Current Density of Oxygen Reaction i_{o2}	1×10^{-8} A/cm^2
Variable	**Initial Value**
y_1	0.35024
y_2	0.4074
1	0.5322
2	0.4254

A general nonlinear DAE system of equations, which are often encountered in process applications, can be described by the following general form of coupled differential and algebraic equations

$$\begin{aligned} \frac{d\mathbf{x}(t)}{dt} &= \mathbf{f}(\mathbf{x},\mathbf{z},\mathbf{u}) \\ \mathbf{g}(\mathbf{x},\mathbf{z},\mathbf{u}) &= \overline{\mathbf{0}} \end{aligned} \qquad \text{----(74)}$$

$\mathbf{x} \in \mathbb{R}^{n_d}$ are the differential states of the process, $\mathbf{z} \in \mathbb{R}^{n_a}$ are the algebraic states of the process and $\mathbf{u} \in \mathbb{R}^{u}$ are the input variables. It is important to note that the initial condition, $\mathbf{x}(0) = \mathbf{x}_0,$ in this case has to be consistent with $\mathbf{z}(0) = \mathbf{z}_0,$ such that the algebraic constraints are satisfied

$$\mathbf{g}(\mathbf{x}_0,\mathbf{z}_0,\mathbf{u}(0)) = \overline{\mathbf{0}}$$

This class of problems need separate treatment while developing numerical solution schemes.

References and cited materials

1. Gilbert Strang, *Linear Algebra and Its Applications* (*4th Ed.*), Wellesley Cambridge Press (2009).

2. Philips, G. M.,Taylor, P. J. ; Theory and Applications of Numerical Analysis (2nd Ed.),Academic Press, 1996.

3. Gourdin,A. and M Boumhrat; Applied Numerical Methods. Prentice Hall (2000).

4. Gupta, S. K.; Numerical Methods for Engineers. Wiley Eastern, New Delhi, 1995.